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Investigation of competitive tar reforming using activated char as catalyst

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Abstract

Syngas tar removal is one of the biggest challenges for the gasification of biomass as a clean energy source. Efforts to understand the reforming mechanism of tar compounds have been continuous during the last decades. Kinetic studies often employ a single tar species, neglecting possible interactions between different tar compounds. On the other hand, char, a by-product from biomass gasification, presents opportunities to catalyze tar reforming. In this work, reforming experiments were conducted in a fixed-bed reactor using syngas with a known mixture of benzene (C_6H_6), toluene (C_7H_8) and naphthalene ($C_{10}H_8$). Hardwood char and an in-situ CO_2-activated hardwood char were used as catalysts. The activated hardwood char exhibited the best reforming capabilities by converting 44% and 90% of the tars at 750 and 850°C, respectively, compared to 24% and 87% tar conversion obtained with the regular hardwood char at 750 and 850°C, respectively. From the experiments, a reduced mechanism model was proposed. This mechanism was used in computational simulations for analysis of the reaction kinetics, including possible catalyst selectivity. It was found that under a range of conditions, the benzene degradation is slower than its formation rate from toluene and naphthalene decomposition. This leads to increases in the benzene fraction at temperatures around 700°C. If the naphthalene and toluene concentrations are sufficient, benzene will accumulate even at high temperatures (around 800°C) regardless of residence times. It can be concluded that when benzene, toluene and naphthalene are present together, char favors the heterogeneous reforming of toluene and naphthalene, with benzene following an homogeneous reforming pathway.

Keywords: "Tar; Syngas; Biomass; Gasification; Char; Catalyst"

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1. Introduction

Biomass as a potentially limitless resource has made biomass gasification a promising technology for energy production with a recurring limitation found in the simultaneous generation of some undesirable compounds (1). An example of these undesirable species are tars, a complex mixture of heavy aromatic hydrocarbons. As tars are responsible of several problems during energy production, a lot of effort has been paid to develop cost-efficient removal methodologies, classified as physical or chemical treatments. Physical treatments are relatively simple, but since the pollutants are transferred to a different phase, additional treatment is required, representing a constrain for the technologies (2). On the other hand, chemical treatments decompose tars to H_2 and CO. This effectively destroys the tars while increasing heating value of the product gas. In this context, tar degradation can undertake different decomposition pathways (3, 4).

Thermal cracking is limited by the high temperatures (over 1000 °C) necessary for the decomposition of the tars (5). Contrarily, catalytic reforming can provide over 95% tar removal at lower temperatures (circa 800 °C). Still, problems exist, as catalysts are easily deactivated either by coke deposition or structural collapse (2, 6–8). On the other hand, char has proven to be a catalyst capable of converting tars almost in their entirety. Moreover, char is naturally produced during the gasification process, therefore, its utilization as catalyst presents opportunities to tackle economic constraints placed in gasification. The removal of tars from biomass gasification syngas represents a problem, as this requires either high temperatures or the use of catalysts, which need to be active, stable and provide enough surface area for reactions. At the same time, as char is produced during gasification, its use as catalyst is attractive to tackle the tar issue.

The use of char as a catalyst has been previously reported a number of times. El-Rub et al (9) employed char to reform naphthalene ($C_{10}H_8$) and analyzed effect factors such as tar concentration, steam concentration and char particle size. Burhenne et al (10) studied benzene (C_6H_6) adsorption and cracking in a char bed during pyrolysis. Fuentes-Cano et al (11) employed a char bed for reforming toluene (C_7H_8) and naphthalene ($C_{10}H_8$), and observed the evolution of the catalyst over time. On the other hand, Jess (12) reported interactions between naphthalene and benzene during reforming with a Ni-based catalyst, leading to decreases in the conversion of benzene in the presence of naphthalene.

There is still a lack of knowledge related to the reforming and the interactions between various tar compounds using char-based catalysts. This work focuses on employing a char bed to catalytically reform a mixture of naphthalene, toluene and benzene present in syngas. Additionally, the possible competition between the tar species for reforming over char is studied. Two different chars are used in the experiments: regular hardwood char and in-situ activated char, both obtained as a by-product from biomass gasification. After the experimental work was done, computational simulations were conducted. Firstly, validation was done by comparing the simulation results with the experiments. Secondly, simulations with different values for residence time, temperatures and concentrations were done to extrapolate the results and gain a better understanding of the tar species reforming and interactions.

Incorporating the char activation in simulations requires experimentation outside of the scope of this work.

Nomenclature

AB	Activated char bed
CB	Char bed
IB	Inert bed
k	Reaction rate constant
k_0	Pre-exponential factor
E_a	Activation energy
R	Ideal gas constant
T	Temperature
X	Conversion
t	Residence time

2. Methodology

2.1. Description of experimental setup, procedure and gas analysis

The experimental setup can be found in **Figure 1**. The reactor is 47 cm long and 2.66 cm in diameter; the actual bed zone was approximately 7 cm tall, with the height adjusted to provide residence times of around 0.5 seconds. Three bed materials were tested: activated hardwood char (AB), regular (without treatment) hardwood char (CB) and silicon carbide (IB). All the bed particles were crushed and sieved to sizes between 200 and 400 µm. Activation of the char was done with a mixture of 35/65 vol. % CO/N_2 for 2 hours. Thermocouples were set at different positions to obtain a temperature profile for the reactor bed. Before the experiments, the reactor was heated to 650 °C and a N_2 stream was injected for at least 1 hour to dry the bed and purge the reactor of any gas. Simulated syngas consisting on CH_4, CO, CO_2, H_2 and N_2 was injected and mixed with steam and 20g/Nm^3 of tars. The volumetric flow rate of the mixture was kept constant at 0.8L/min. The tar proportions were 15.53, 23.13 and 61.32 wt. % for naphthalene, toluene and benzene, respectively. Experiments were done at temperatures of 650, 750 and 850 °C.

Analysis of the gases at the outlet of the reactor was done with a Gas Chromatographer for the tar measurements and a gas analyzer for the dry permanent gases. Before analysis of the permanent gases, the stream was passed through a cold trap for recovery of the tar species.

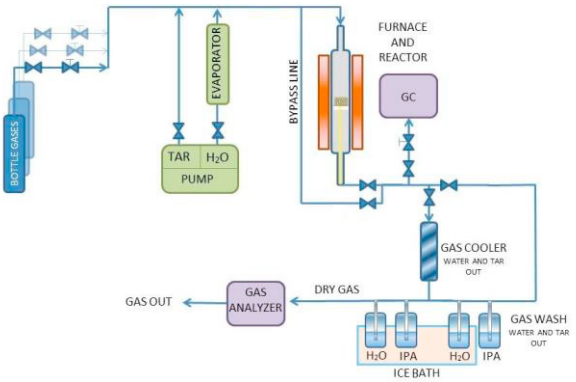

Figure 1. Reactor setup used in the experiments.

2.2. Determination of kinetic parameters

Plug-flow behaviour and negligible diffusion in the catalyst particles were assumed for determining the kinetic parameters. A first-order rate law was utilized for all the tar species, with the reaction rate constant being:

$$k = k_0 e^{-Ea/RT} \tag{1}$$

Where k is the reaction rate constant, k_0 is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant and T is temperature. Tar conversion was defined in Eq. 2, and the rate constant was calculated with Eq. 3.

$$X = \frac{C_{A,in} - C_{A,out}}{C_{A,in}} \tag{2}$$

$$k = \frac{-\ln(1-X)}{t} \tag{3}$$

Where X is the conversion, $C_{A,\,in}$ and $C_{A,\,out}$ are the concentrations of species *"A"* at the inlet and outlet of the reactor, respectively, and t is the residence time inside the catalyst bed. The average time is defined as:

$$t = \frac{V}{Q} \tag{4}$$

Where V is the bed volume and Q is the gas volumetric flow rate.

2.3 Computational simulations

Simulations to reproduce the experiments were done with a 1D model using the chemistry suite Cantera (13). Validation of the kinetic parameters was done by comparing experiments with simulation results.

3. Results and discussion

3.1. Catalytic conversion of tars

Results from the tar conversions obtained using the char bed (CB), the activated char bed (AB) and the inert bed (IB) can be seen in **Figure 2**. **Figure 2a** illustrates the total tar conversion as a function of temperature in different beds, whereas **Figure 2b** shows the normalized mole fractions of some of the reforming products using different beds at different temperatures. Experiments with AB provide the best conversion, followed by CB. As expected. the "blank" IB provided negligible tar conversion. With any of the chars about 80% of the benzene was reformed at 850 °C. In contrast, previous studies which employed benzene as the only model tar, almost 100% was converted at 850 °C under pyrolysis conditions (10). The lower conversion may be attributed to the affinity of toluene and naphthalene for adsorption in the char surface for heterogeneous reforming and coke formation. In this work the benzene follows an heterogeneous reforming pathway while the toluene and naphthalene interact with the char surface, as it is known that heavy molecules have affinity for deposition in catalysts (14). In the reference (10), the benzene may be adsorbed and reformed heterogeneously in the char catalyst. On the other hand, similarities in the product composition (found in **Figure 2b**) with experiments with the two chars indicate that increases in the tar conversion from the CB to the AB are most likely due to the increase in surface area, and not by the addition of formation of functional groups in the AB surface during activation.

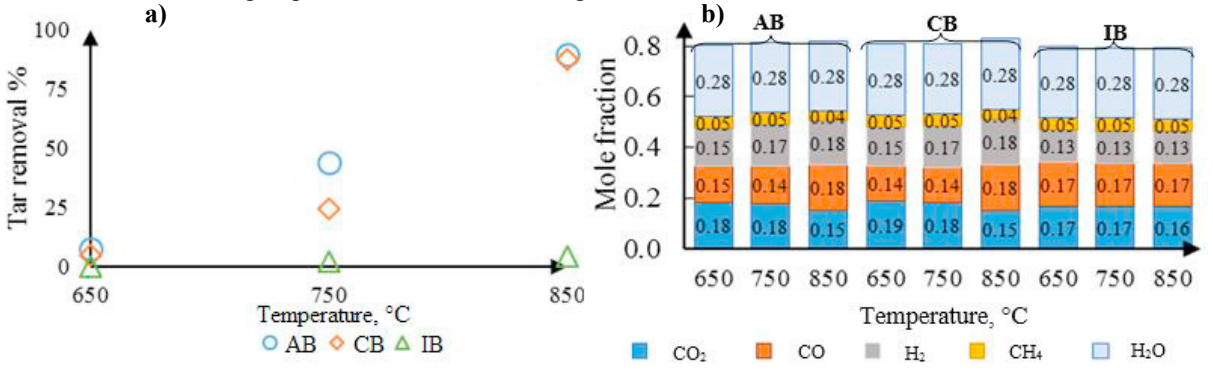

Figure 2. Products from the conversion of tars with different bed materials. a) Total tar conversion percentages b) Product mole fractions.

3.2. Kinetic model for tar reforming

The reduced mechanism found in **Table 1** was proposed based in the observed tar conversions and product compositions. These kinetic parameters were employed in simulations using Cantera (13). Results from these are shown in **Figure 3**, where **3a** presents the products from reforming in the AB and **3b** presents the products using the

CB. There are discrepancies in the H_2 and CO content from the simulations due to bed gasification reactions not being accounted in the reduced mechanism. Still, percentage differences between values obtained from simulations and experiments are less than 15%.

Table 1. Reduced mechanism for catalytic tar reforming

Reaction	k_0		E_a, kJ/mol		r^2	
	AB	CB	AB	CB	AB	CB
$C_6H_6 + 6H_2O \rightarrow 6CO + 9H_2$	$1.98x10^7$	$9.79x10^7$	144	162	0.99	0.95
$C_7H_8 + H_2O \rightarrow C_6H_6 + CO + 2H_2$	$3.27x10^6$	$2.51x10^8$	118	160	0.99	0.99
$C_{10}H_8 + 4H_2O \rightarrow C_6H_6 + 4CO + 5H_2$	$2.68x10^5$	$2.21x10^8$	95.7	159	0.99	0.99

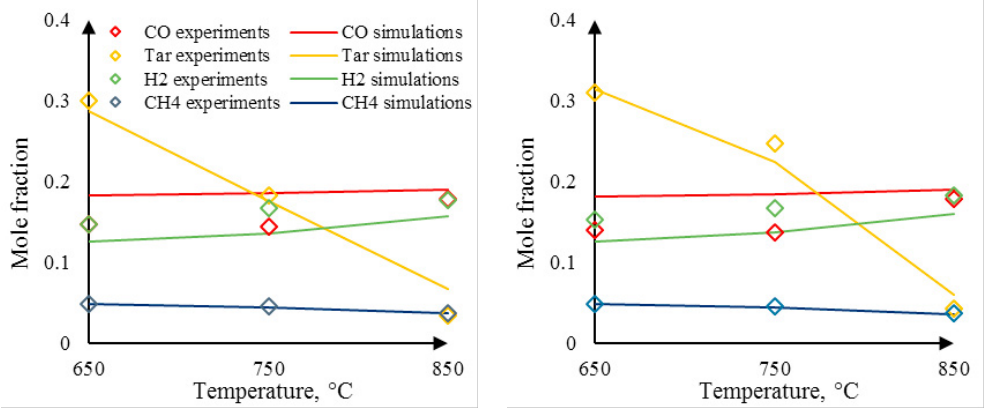

Figure 3. Comparison of results from experiments and simulations. a) Activated char as a catalyst b) Regular char as a catalyst.

3.3. Effect of temperature, tar concentration and residence time in tar reforming

Simulations were done to analyze the influence of reaction time, tar concentration and temperature in the reaction yields. Some of the results can be found in **Figure 4**. In the figures, values lower than 1 imply a decrease in the mole fraction, and vice versa. **Figures 4a**, **c** and **e** are from simulations with total tar concentration of 20g/Nm^3 (3.106, 4.626 and 12.264 g/Nm^3 for naphthalene, toluene and benzene, respectively), whereas **Figures 4b**, **d** and **f** are obtained from simulations with total tar concentrations of 40g/Nm^3 (6.212, 9.252 and 24.528 g/Nm^3 for naphthalene, toluene and benzene, respectively). This was done to observe the influence of the benzene formation from toluene and naphthalene, and its subsequent effect in benzene degradation. Results from **Figure 4a, b, c** and **d** agree with previous reports (9,11) where the naphthalene and toluene concentration has a negligible effect in their conversions. **Figure 4e** shows how, regardless of residence time, benzene requires temperatures of around 690°C to get noticeable conversion. Moreover, from **Figure 4f**, when the tar concentration is duplicated, at temperatures below 750 °C the benzene fraction increases instead of decreasing. This occurs from the decomposition of the other tars whose decomposition reaction rate is much higher at these temperatures; at less than 800 °C the rate of benzene formation increases with residence time.

Additional simulations were conducted to analyze the effects of temperature and residence time for the catalytic conversion of benzene with different concentrations of toluene and naphthalene using both types of char. The benzene concentration was fixed and the toluene/naphthalene concentrations were multiplied "n" number of times. Results of these simulations are found in **Figure 5.** Figures **5a**, **5b**, **5c** and **5d** correspond to 650, 750, 850 and 950 °C, respectively. In the figures, the lines correspond to the benzene fraction while the symbols represent the toluene and naphthalene fraction; this is done to appreciate the conversion of the heavier hydrocarbons to benzene. In a way similar to **Figure 4e** and **4f**, from **Figure 5a** it can be seen that at the experiment conditions and for both chars, the benzene conversion is independent of residence time. Increasing the toluene and naphthalene then leads to benzene accumulation. When the temperature is increased to 750 °C (**Figure 5b**) and at different concentrations for the

heavier tars, when using the AB, the benzene first increases before decreasing at the moment where the concentration of toluene and benzene hits about 25% its initial value, even when the concentration of the heavier tars is increased tenfold-wise. This is not the case with the CB, as even after 1 second residence time the benzene concentration reaches a plateau, meaning that longer residence times are necessary. This "threshold" toluene/naphthalene concentration can be further observed at 850 °C (**Figure 5c**). The toluene and naphthalene are quickly decomposed to about 30% its initial value in 0.1 seconds residence time without any plateau in the benzene concentration. Moreover, at 850 °C more than 80% conversion of benzene can be obtained for every case after about 1 second residence time. At 950 °C (**Figure 5d**) complete conversion of benzene is obtained after 0.3 seconds using the activated char and 0.4 seconds using the regular char, regardless of the concentration of the tars.

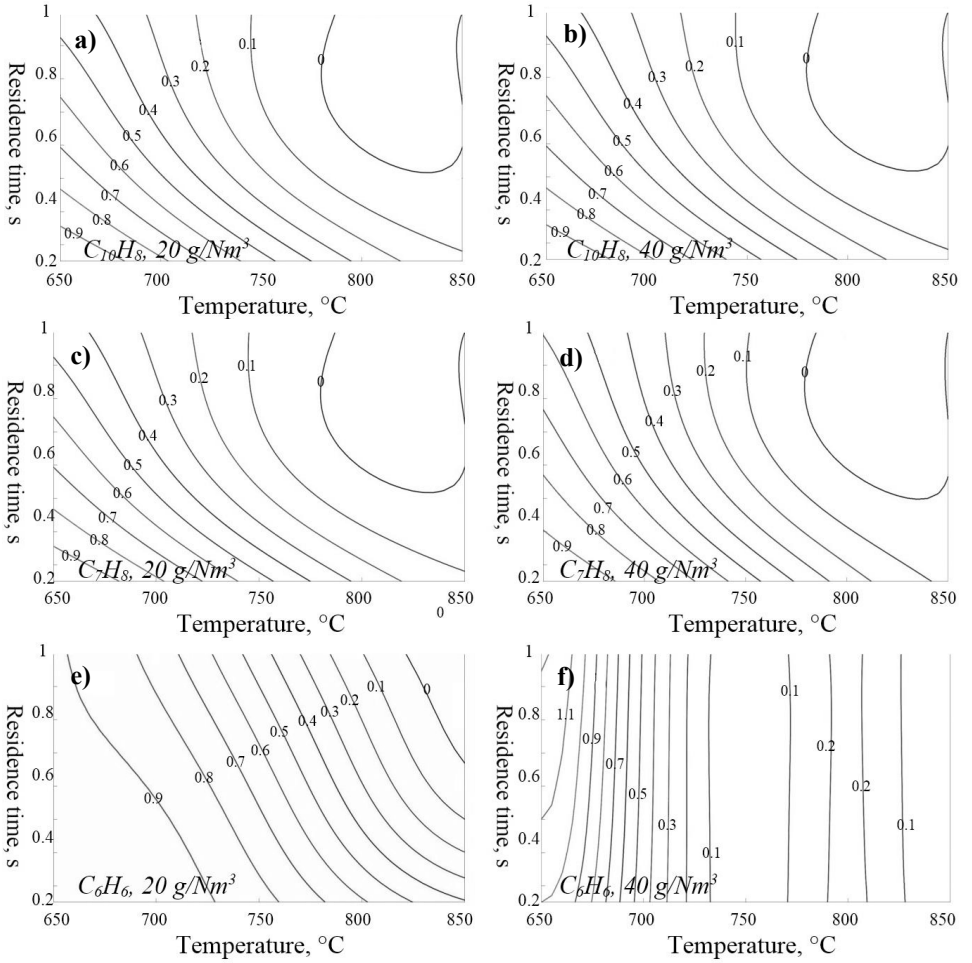

Figure 4. Contours of the normalized mole fraction as a function of temperature (°C) and residence time (s).

From the experiments and simulations it can be seen that for complete removal, benzene requires temperatures of about 950 °C which are high when compared to 850 °C, necessary to remove the other tars. This behavior can be associated to benzene following catalytic cracking, compared to catalytic reforming in the char surface. Toluene and naphthalene may be favored for deposition as coke in the char followed by coke reforming with CO_2/steam. This goes in agreements with previous reports where it was found that heavier molecules are more prone for coke deposition in the catalyst surface, deposition rate being a function of surface area (14,15).

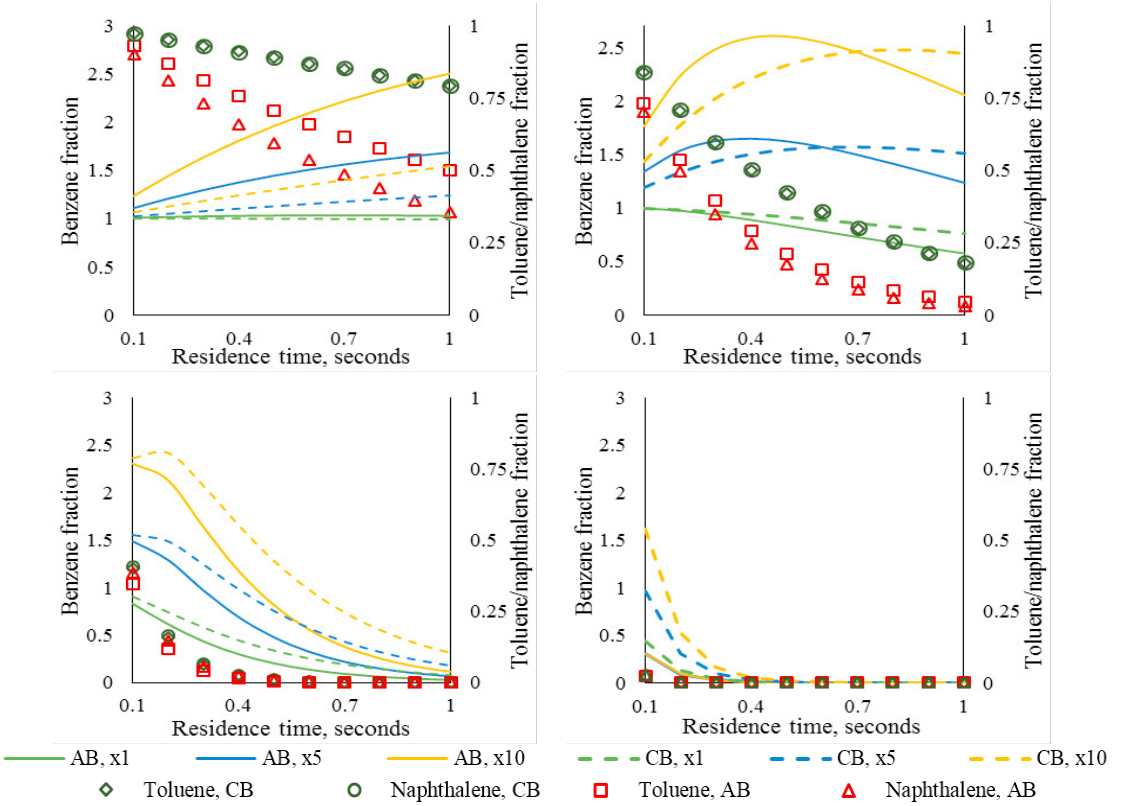

Figure 5. Normalized benzene mole fraction at fixed temperatures as a function of toluene and naphthalene concentrations and residence time (s). The plots correspond to the following temperatures: a) 650 °C, b) 750 °C, c) 850 °C and d) 950°C.

4. Conclusions

Experiments and simulations were done to study the conversion of a mixture of tar model compounds using char as a catalyst. From experimental and numerical results, the following can be concluded:

- Physical activation with CO_2 at 750 °C for 2 hours increased the char catalytic activity for tar reforming when the reforming experiments were conducted at temperatures of 650 and 750°C. At 850 °C, both chars provided about 99% conversion for toluene and naphthalene and about 85% conversion for benzene.
- Comparison with previous reports lead to the assumption that when mixed with heavier tars, benzene is favored by thermal cracking. Hence, higher temperatures are necessary for benzene decomposition when compared to toluene and naphthalene. The benzene is not as problematic as heavier hydrocarbons, thus even if its reforming efficiency is relatively low, char is overall a promising catalyst for reforming.
- Char as a catalyst favors the conversion of naphthalene and toluene. If present together with toluene or naphthalene, catalytic reforming of benzene is only noticeable at temperatures above 750 °C regardless of residence times. At lower temperatures, increasing residence time will lead to benzene formation. After the concentration of toluene and naphthalene is reduced below a certain value, these will have no further effect in the conversion of benzene.
- At temperatures of 950°C and residence times of more than 3 seconds, benzene can be completely degraded regardless of the presence of toluene and naphthalene.

Future work is necessary to understand the physicochemical interactions between the gases and the catalyst surface, as this is not well known and is subject to debate. Besides differences of selectivity between the tars, there may be additional competition for adsorption between the tars and reforming agents on active sites.

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